Removal of Heavy Metal Ions using Surface-Modified Polysulfone Membrane with Amphiphilic Hyperbranched Poly(amidoamine)

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1. Introduction

The discharge of heavy metals into water has caused a serious environmental problem due to their high toxicity and the potential of bio-accumulation [1]. A lot of efforts have been made for removal of heavy metals from contaminated wastewater and reported in literatures [2].

Nevertheless, traditional physicochemical methods are still widely used for the treatment of water contaminated by heavy metals, such as the chemical precipitation, the adsorption, the ion-exchange and the RO (reverse osmosis) processes. The treatment methods can differ according to the form of metals. The filtration techniques can easily separate the metal in their colloidal state or particle state. On the other hand, for metal ions in aqueous solution, techniques like ion-exchange and RO should be used to remove the ions. RO techniques are very efficient in terms of elimination of heavy metal ions but they are capital-intensive and their performances dramatically decrease by membrane fouling.

In this study, we prepared and used surface-modified polysulfone (PSf) membranes with amphiphilic polymers, palmitoyl chloride functionalized hyperbranched poly(amidoamine)s (A-HYPAM), as a technique for removal of heavy metal ions from aqueous solution. Cu(II) was selected as a heavy metal ion model. The A-HYPAM was expected to facilitate formation of stabilized attractive association with heavy metal ions [3]. The membrane was successfully fabricated by blending PSf solution with A-HYPAM and followed by solidifying the blend via phase inversion process. The chemical composition of the membrane surface was characterized by XPS and ATR-FTIR spectroscopy. It was revealed that A-HYPAM was located at the surface of membrane. The morphology of the membrane and the amount of the A-HYPAM introduced were investigated by FE-SEM and TGA, respectively. The binding capacity of the membrane for Cu(II) was investigated by carrying out filtration at pH 5. The concentrations of the solutions at before and after the filtration were evaluated by UV-Vis spectroscopy for confirmation of the retained metal ions. In addition, the membrane showed its reusability since A-HYPAM immobilized on the membrane surface binds and releases Cu(II) in water under various pH conditions, repeatedly. Therefore, the surface-modified membrane is one of promising candidates as a highly efficient and reusable material for removal of heavy metal ions in wastewater treatment technology.

2. Experimental

HYPAM was synthesized by a simple one-pot method.[2]

To modify the HYPAM to be amphiphilic, 0.76 mL of palmitoyl chloride dissolved in 10 mL chloroform solution was slowly added to a solution of 14.5 wt% HYPAM in chloroform and 0.70 mL of triethylamine. The mixture was stirred at 35 ℃ for 24 h, and then washed with deionized water several times. The lower phase was separated and dried with anhydrous magnesium sulfate ($MgSO_4$) and then filtrated. Subsequently, the filtrate was precipitated in methanol. After the precipitate was dried under vacuum at 50 ℃ for 24 h, the amphiphilic HYPAM (a-HYPAM) was obtained.

To fabricate HYPAM-anchored membrane, polysulfone (PSf) was dissolved in N-methyl-2-pyrrolidinone (NMP) to make 15 wt% polymer solutions. The PSf solution and

the a-HYPAM were mixed together in a given composition (1, 4, 8 wt% a-HYPAM vs. PSf solution) to make dope solutions. The dope solutions were cast on a glass substrate with a 120 μm applicator and immersed in the bath (5 wt% NMP aqueous solution) immediately. After peeling from the substrate, the membranes were rinsed with deionized water several times and stored in water before use.[3]

3. Results and discussion

The chemical structure of the HYPAM was characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR. The IR absorptions at 3300 (NH_2 stretch) and 1557 cm^{-1} (NH_2 bend) were observed. In addition, a relatively weak peak at 1730 (ester C=O stretch) and a strong peak at 1650 cm^{-1} (amide C=O stretch) were observed.

The analysis of the a-HYPAM was conducted by FT-IR and ^{1}H-NMR spectra. In FT-IR spectra, a long alkyl chain peak was observed in the range of 2850–3000 cm^{-1}. In ^{1}H-NMR ($CDCl_3$) spectra, 0.88 ($-CH_3$) and 1.25 [$-(CH_2)_{13}-$] peaks appeared.

PSf and 1, 4, 8 wt% HYPAM-anchored membranes (PSf-M, HYP-M1, HYP-M4, HYP-M8) were characterized by XPS, ATR-IR to confirm the presence of a-HYPAM on the membrane surface. Figure 1 shows XPS curves of the membrane surface. In the case of HYP-M series, signal observed at 530.1 eV was attributed to the oxygen of carbonyl group which was not observed in PSf-M.

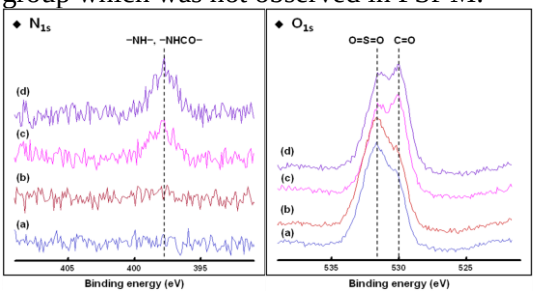

Figure 1. XPS curves of a) PSf-M, b) HYP-M1, c) HYP-M4, d) HYP-M8 surfaces.

The signal observed at 397.9 eV was attributed to the nitrogen of amine and amide which were larger in order of the greater content of a-HYPAM.

ATR-IR spectra of the membranes displayed the characteristic peaks of a-HYPAM. The peak at 3300 cm^{-1} (N-H stretch) and 1650 cm^{-1} (amide C=O stretch) became larger in accordance of the content of a-HYPAM. Moreover, the peak in the range of 2850–3000 cm^{-1} (C-H stretch) became larger due to the increase in the contents.

The contents of a-HYPAM anchored on membranes were measured from TGA curves. Figure 2 shows the weight loss of the four membranes when heated from 50 to 700 ℃. The a-HYPAM contents, estimated from comparing the residual weight of (b), (c), and (d) with that of (a) at 500 ℃, are 5, 19, and 34 wt%.

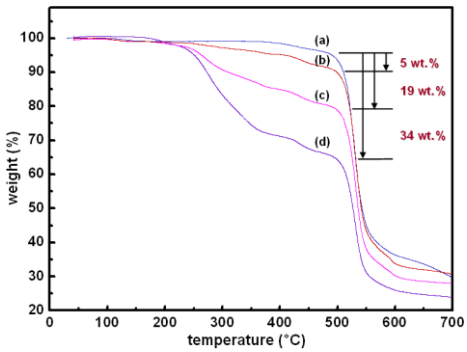

Figure 2. TGA curves of a) PSf-M, b) HYP-M1, c) HYP-M4, d) HYP-M8.

Fig. 3 shows FE-SEM images of both surfaces and the cross-section of the membrane. The water-contacting (front) surface had cracks, and the glass-contacting (back) surface had pores. The pore size observed on the back surface of the four membranes was in the range of 10–100 nm. No significant change of morphology was observed with an increase in the content of a-HYPAM.

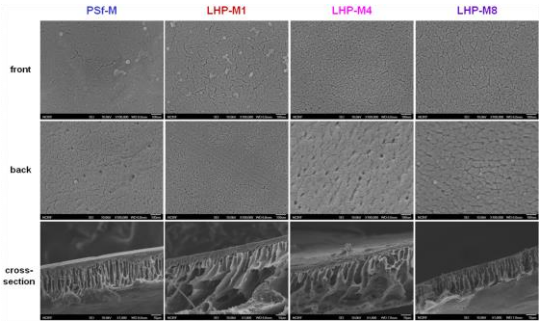

Figure 3. FE-SEM images of PSf-M, HYP-M1, HYP-M4, and HYP-M8.

4. Conclusions

In this study, we focused on the preparation

of HYPAM-anchored membrane which is a promising candidate for removal of heavy metal ions from wastewater. The HYPAM-anchored membrane has been fabricated and confirmed by ATR-IR and XPS. The contents of a-HYPAM present on membranes have been measured by TGA and have been 5, 19, and 34 wt% in order of HYP-M1, HYP-M4, and HYP-M8. No significant change of the membrane morphology has been observed by FE-SEM images. Consequently, the results of this study indicate that HYPAM-anchored membrane can be successfully fabricated for removal of heavy metal ions in water treatment.

Acknowledgement: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (R11-2005-065).

References

1. W. Stumm, J. J. Morgan, *Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters*; John Wiley & Sons: New York, (1996).
2. N. Perignon, A.-F. Mingotaud, J.-D. Marty, R.-L. Isabeelle and C. Mingotaud, *Chemistry of Materials*, 16, 4856 (2004).
3. T. Hasegawa, Y. Iwasaki and K. Ishihara, *Biomaterials*, 22, 243 (2001).